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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: COATING COMPOSITION INCLUDING A UV-DEBLOCKABLE BASIC CATALYST

(57) Abstract

A coating composition is provided which is based upon (A) an activated unsaturated group-containing compound, (B) an activated CH group-containing compound and (C) a basic catalyst, wherein the basic catalyst is blocked with an acidic compound whereby the so-blocked catalyst becomes unblocked under the influence of UV light. These coating compositions possess extended potlife, good curing speed, and a good balance of physical and mechanical properties making them especially well-suited for a variety of coatings uses such as in paint, impregnating, sealing and bonding compositions.

amine - guanidine, hydroxypyrimidines, diaza-, imidazolines
 ammonium
 phosphane

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Coating Composition Including a UV-Deblockable Basic Catalyst

Background of the Invention

5 The present invention relates generally to coating compositions based upon (A) compounds containing activated unsaturated groups and (B) compounds containing activated CH groups.

10 These compositions are, in general, known from a number of references including US2759913, DE-PS-835809, US4871822 (EP-A-0160824), US4602061, US4408018, US4217396 (GB-A-2048913) and EP-A-0448154, all of which are incorporated by reference herein for all purposes.

15 For example, US2759913 and US4871822 generally disclose a composition of the above type which may be cured at ambient and elevated temperatures. More specifically, these references generally describe, as component (A), compounds containing at least two activated ethylenic double bonds and, as component (B), a wide variety of compounds including those containing at least two activated methylene and/or monosubstituted methylene groups.

20 US4602061 discloses a similar composition except that, as component (B), are specifically mentioned malonic group-containing oligomeric and polymeric esters.

25 US4408018 and US4217396 again disclose similar compositions except that, as component (B), are specifically mentioned acetoacetate groups-containing compounds.

30 It is also known from these references, and in general, that components (A) and (B) can react rapidly in the presence of (C) a basic catalyst via a Michael addition. For this reason, it has not generally been possible to formulate one-pack coatings based upon this combination of components due to a too short potlife.

5 In addition, because such catalyst is basic it has a tendency to become deactivated in the presence of certain acidic additives (e.g., certain pigments) or when the composition is applied to substrates having an acidic nature. This effect can be overcome by increasing the amount of catalyst; however, an already short potlife may be further shortened. The potlife problem is further exacerbated by the use of elevated temperatures.

10 One alternative for overcoming this problem in thermosetting applications is described in aforementioned EP-A-0448154, in which the basic catalyst is blocked with a particular carboxylic acid which is volatile and/or undergoes decarboxylation under curing conditions. While providing good results for elevated cure conditions, this system is not generally applicable at ambient temperatures. It is, therefore, difficult to utilize these systems for heat sensitive
15 substrates such as wood and thermoplastic polymers, as well as in industrial and non-industrial applications like decorative coatings and refinish paints.

20 An ambient temperature alternative for the systems described in EP-A-0448154, therefore, would be desirable.

Summary of the Invention

25 The present invention provides such an alternative by utilizing a system which is curable under the influence of UV light.

30 More specifically, the present invention relates to a coating composition comprising (A) an activated unsaturated group-containing compound, (B) an activated CH group-containing compound and (C) a basic catalyst, characterized in that the basic catalyst (C) is blocked with an acidic compound whereby the so-blocked catalyst becomes unblocked under the influence of UV light having a wavelength in the range from 250-500 nm.

It should be noted that UV-deblockable basic catalysts are in general known from US4301186, US4369206, DE-A-2940333 and DE-A-2940332, all of which are incorporated by reference herein for all purposes as if fully set forth. The suitability of such blocked catalysts for use in Michael addition curing coating systems, however, is not evident from any of the above-mentioned disclosures.

5

The coating compositions in accordance with the present invention are in general suitable for a variety of coatings uses, for example, as paint, impregnating, sealing and bonding compositions. They are especially suited for use as semi-one pack decorative coatings and as clearcoats in basecoat/clearcoat systems for refinish applications (e.g., for automotive refinishes).

10

These coating compositions possess extended potlife, good curing speed upon exposure to UV light (wavelength of 250-500 nm), and a good balance of physical and mechanical properties making them especially well suited for the aforementioned uses.

15

These and other features and advantages of the present invention will be more readily understood by those skilled in the art from a reading of the following detailed description.

20

Detailed Description of the Preferred Embodiments

As mentioned earlier, the coating compositions in accordance with the present invention are based upon (A) activated unsaturated group-containing compounds, (B) activated CH group-containing compounds and (C) a basic catalyst, which basic catalyst is blocked in a manner more fully described below.

25

30

(A) Activated Unsaturated Group-Containing Compounds

As suitable compounds containing activated unsaturated groups may generally be mentioned ethylenically unsaturated compounds in which the carbon-carbon double bond is activated by a carbonyl group in the α -position. As representative examples of such may be mentioned those compounds disclosed in previously incorporated US2759913 (see especially column 6, line 35 through column 7, line 45), DE-PS-835809 (see especially column 3, lines 16-41), US4871822 (see especially column 2, line 14 through column 4, line 14), US4602061 (see especially column 3, line 14 through column 4, line 14), US4408018 (see especially column 2, lines 19-68), US4217396 (see especially column 1, line 60 through column 2, line 64) and EP-A-0448154 (see especially page 2, line 53 through page 3, line 28).

As a first preferred example may be mentioned the (meth)acrylic esters of compounds containing 1-6 hydroxyl groups and 1-20 carbon atoms. Instead of or in addition to (meth)acrylic acid may be used, for example, crotonic acid and cinnamic acid. These esters may optionally contain hydroxyl groups. Especially preferred examples include hexane diol diacrylate, trimethylol propane triacrylate and pentaerythritol triacrylate.

As a second preferred example may be mentioned polyesters based upon maleic, fumaric and/or itaconic acid (and maleic and itaconic anhydride), and di- or polyvalent hydroxyl compounds, optionally including a monovalent hydroxyl and/or carboxyl compound.

As a third preferred example may be mentioned polyester and/or alkyd resins containing pendant activated unsaturated groups. These include, for example, urethane (meth)acrylates obtained by reaction of a polyisocyanate with an hydroxyl group-containing (meth)acrylic ester, e.g., an hydroxyalkyl ester of (meth)acrylic acid or a compound prepared by esterification of a polyhydroxyl compound with less than a

stoichiometric amount of (meth)acrylic acid; polyether (meth)acrylates obtained by esterification of an hydroxyl group-containing polyether with (meth)acrylic acid; polyfunctional (meth)acrylates obtained by reaction of an hydroxyalkyl (meth)acrylate with a polycarboxylic acid and/or a polyamino resin; poly(meth)acrylates obtained by reaction of (meth)acrylic acid with an epoxy resin; and polyalkylmaleates obtained by reaction of a monoalkylmaleate ester with an epoxy resin and/or an hydroxy functional oligomer or polymer.

Especially preferred of the activated unsaturated group-containing compounds are the aforementioned poly(meth)acrylates obtained by the reaction of (meth)acrylic acid with an epoxy resin.

It is also especially preferred that the acid value of the activated unsaturated group-containing compounds be about 2 or less.

As exemplified by the previously incorporated references, these and other activated unsaturated group-containing compounds, and their methods of production, are generally known to those skilled in the art, and need no further explanation here.

(B) Activated CH Group-Containing Compounds

As suitable compounds containing activated CH groups may be mentioned a wide variety of compounds as generally disclosed in previously incorporated US4871822 (see especially column 4, lines 15-28), which compounds contain a methylene and/or monosubstituted methylene group in the α -position to two activating groups such as, for example, carbonyl, cyano, sulfoxide and/or nitro groups. Preferred of these are compounds containing a methylene group in the α -position to two carbonyl groups, such as malonate and/or acetoacetate group-containing compounds.

As preferred examples of malonate group-containing compounds may be mentioned malonic acid esters as disclosed in previously incorporated US2759913 (see especially column 8, lines 51-52), and malonate group-containing oligomeric and polymeric compounds as disclosed in previously incorporated US4602061 (see especially column 1, line 10 through column 2, line 13). Preferred of these are the oligomeric and/or polymeric malonate group-containing compounds such as, for example, polyurethanes, polyesters, polyacrylates, epoxy resins, polyamides and polyvinyl resins containing malonate groups in the main chain, pendant or both.

The malonate group-containing polyurethanes may be obtained, for example, by reacting a polyisocyanate with an hydroxyl group-containing ester of a polyol and malonic acid, or by esterification or transesterification of an hydroxy functional polyurethane with malonic acid or a dialkylmalonate.

The malonate group-containing polyesters may be obtained, for example, by the polycondensation of malonic acid, an alkyl malonic acid (such as ethyl malonic acid), a mono- or dialkyl ester of such a malonic acid, and/or the reaction product of a malonic ester and an alkyl (meth)acrylate, optionally with other di- or polycarboxylic acids; with di- and/or higher functional hydroxy compounds; and, optionally monofunctional hydroxy and/or carboxyl compounds.

The malonate group-containing epoxy esters may be obtained, for example, by esterifying an epoxy resin with malonic acid or a malonic monoester, or by transesterification with a dialkyl malonate, optionally with other carboxylic acids and derivatives thereof.

The malonate group-containing polyamides may be obtained, for example, in the same manner as the polyesters, wherein at least a part of the hydroxy compound is replaced with a mono- and/or polyvalent primary and/or secondary amine.

Other malonate group-containing polymers may be obtained by the transesterification of an excess of a dialkyl malonate with an hydroxy-functional polymer such as, for example, a vinyl alcohol/styrene copolymer. In this manner, a polymer with malonate group-containing side-chains may be formed. Any excess dialkyl malonate may be removed under reduced pressure or, optionally, be used as a reactive solvent.

Use may also be made of these malonate group-containing compounds in which the malonic acid structural unit is cyclized, for example, by formaldehyde, acetaldehyde, acetone or cyclohexanone.

Especially preferred of the malonate group-containing compounds for use with the present invention are the malonate group-containing oligomeric esters, polyesters, polyurethanes and epoxy esters containing 2-100, more preferably 2-20, malonate groups per molecule. It is also especially preferred that such malonate group-containing compounds have a number average molecular weight (M_n) in the range of from about 250 to about 3000, and an acid number of about 2 or less.

As preferred examples of acetoacetate group-containing compounds may be mentioned acetoacetic esters as disclosed in previously incorporated US2759913 (see especially column 8, lines 53-54), diacetoacetate compounds as disclosed in previously incorporated US4217396 (see especially column 2, line 65 through column 3, line 27), and acetoacetate group-containing oligomeric and polymeric compounds as disclosed in previously incorporated US4408018 (see especially column 1, line 51 through column 2, line 6). Preferred of these are the oligomeric and/or polymeric acetoacetate group-containing compounds.

Suitable acetoacetate group-containing oligomeric and polymeric compounds can be obtained, for example, from polyalcohols and/or hydroxy-functional polyether, polyester, polyacrylate, vinyl and epoxy

oligomers and polymers by reaction with diketene or transesterification with an alkyl acetoacetate. Such compounds may also be obtained by copolymerization of an acetoacetate functional acrylic monomer with other vinyl- and/or acrylic-functional monomers.

5 Especially preferred of the acetoacetate group-containing compounds for use with the present invention are the acetoacetate group-containing oligomers and polymers containing at least 2 acetoacetate groups. It is also especially preferred that such
10 acetoacetate group-containing compounds should have an Mn in the range of from about 234 to about 30000, and an acid number of about 2 or less.

Compounds containing both malonate and acetoacetate groups in the same molecule are also suitable and can be obtained, for example, by a
15 Michael reaction between a malonate functional polyester and an acetoacetate functional acrylic compound (e.g., acetoacetoxyethyl acrylate). Additionally, physical mixtures of malonate and acetoacetate group-containing compounds are suitable. Alkylacetoacetates can, in addition, be used as reactive diluents.

20 Optionally, the activated CH groups-containing compounds may be utilized in enamine form such as disclosed in EP-A-0420133, which is incorporated by reference herein for all purposes as if fully set forth.

25 Again as exemplified by the previously incorporated references, these and other malonate and/or acetoacetate group-containing compounds, and their methods of production, are generally known to those skilled in the art, and need no further explanation here.

30 As mentioned earlier, the aforescribed components (A) and (B) react with each other through a Michael addition, in which the activated CH group of component (B) adds to one of the carbon atoms of the

activated unsaturated group of component (A). Components (A) and (B) are preferably contained in the coating compositions in an amount such that the ratio of the number of activated CH groups to the number of activated unsaturated groups is in the range of about 0,25 to about 4,0, more preferably in the range of about 0,5 to about 2,0.

5

(C) Blocked Basic Catalysts

As indicated earlier, the blocked basic catalysts suitable for use with the present coating compositions are blocked with an acidic compound, whereby the so-blocked catalyst becomes unblocked under the influence of UV light having a wavelength in the range from 250-500 nm.

10

As suitable basic catalysts for the Michael addition of components (A) and (B) may be mentioned a wide variety of well-known amine, ammonium and phosphane compounds disclosed in the previously incorporated references.

15

As preferred amine catalysts may be mentioned those of the amidine type, for example, tetramethyl guanidine, 1,4-dihydropyrimidines, 1,8-diaza-bicyclo[5.4.0]undec-7-ene, 1,4-diaza-bicyclo[2.2.2]octane and 2-alkyl-N-alkyl imidazolines.

20

As preferred ammonium catalysts may be mentioned quaternary ammonium compounds, for example, quaternary ammonium hydroxides such as tetrabutyl ammonium hydroxide; quaternary ammonium alkoxides such as benzyltrimethyl ammonium methoxide and dilauryldimethyl ammonium methoxide; and quaternary ammonium carbanions such as benzyltrimethyl ammonium acetyl acetate.

25

As preferred phosphane compounds may be mentioned those disclosed in previously incorporated US4871822 (column 7, line 48 through column 8, line 2), and particularly the tertiary phosphanes

30

disclosed therein. As specific preferred examples may be mentioned tris(hydroxymethyl)phosphane, triphenylphosphane and tris(p-tolyl)phosphane.

5 These basic catalysts (unblocked) are generally utilized in amounts ranging from about 0,05 wt% to about 3,0 wt%, preferably from about 0,1 wt% to about 1,0 wt%, based upon the combined weight of components (A) and (B). C

10 Suitable blocking agents for these basic catalysts comprise acidic compounds selected from:

- (a) α -keto carboxylic acids,
- (b) aromatic or N-heterocyclic substituted formic, acetic and oxyacetic acids, and
- (c) halide compounds.

15 As mentioned earlier, suitable α -keto carboxylic acid blocking agents are known from previously incorporated US4301186 (column 1 line 35 through column 2, line 58) and US4369206 (column 1, line 36 through column 2, line 37). As preferred examples may be
20 mentioned phenyl glyoxylic acid, 1-naphtyl glyoxylic acid, pyruvic acid and benzylidene pyruvic acid.

25 Suitable aromatic or N-heterocyclic substituted formic, acetic and oxyacetic acid blocking agents are known from previously incorporated DE-A-2940333 (page 7, line 15 through page 8, line 15). As preferred examples may be mentioned phenyl acetic acid, 1-naphtyl acetic acid and 9-anthracene carboxylic acid.

30 Suitable halide blocking agents are generally known from DE-A-2940332. Preferred are the anions chloride, bromide and iodide. The halide blocking agents, however, are in general less preferred because a low molecular weight halogenide may be released upon unblocking of the catalyst.

5 The acidic compound is preferably utilized in an amount of from about 10 to about 125, more preferably from about 25 to about 125, and especially from about 50 to about 100, equivalent percent required to neutralize the basic catalyst. Within these ratios, the potlife of the composition can be readily varied, for example, between $\frac{1}{2}$ hour at 20°C to more than 6 weeks at 50°C.

10 The basic catalyst and blocking agent can be mixed in situ and added to the composition in quantities to result in the desired ratio as set forth above. Alternatively, a salt of the catalyst and blocking agent can be pre-prepared and added to the composition.

15 The curing of the above-described coating compositions is preferably carried out at ambient temperatures (e.g., 10-30°C) under the influence of UV light of a wavelength 250-500 nm, which can be from a UV source or even daylight.

20 Depending upon the field of application, the coating compositions in accordance with the present invention may optionally contain one or more pigments, dyes and usual intermediary agents, additives and/or solvents. Examples of suitable inert organic solvents include esters, ketones aromatic and aliphatic hydrocarbons. Examples of suitable reactive organic solvents include dimethyl malonate, diethyl malonate, ethyl acetoacetate and 2-ethylhexyl acrylate.

25 As examples of preferred additives may may be mentioned minor amounts of a co-binder not containing activated unsaturated or CH groups, for example, cellulose acetate butyrate, acrylic, epoxy and polyester resins. As is known to one skilled in the art, these co-binders are commonly utilized in the coatings industry to modify certain properties such as drying speed and adhesion to substrates.

30

As another preferred additive may be mentioned a UV sensitizer, such as anthracene, which is used to increase the amount of UV light absorbed by the coating composition.

5 As mentioned earlier, the coating compositions in accordance with the present invention are suitable for a variety of coatings uses, for example, as paint, impregnating, sealing and bonding compositions. A preferred application is as a semi one-pack decorative coating.

10 Another preferred application is as a clearcoat in a basecoat/clearcoat system for refinish applications (e.g., automobile refinish). Suitable basecoats for use in such systems are in general well-known in the art.

15 These coating compositions may be applied to a substrate in any convenient manner such as, for example, by brushing, spraying or dipping. Suitable substrates include metals, wood, board, plastics and leather.

20 The foregoing more general discussion of the present invention will be further illustrated by the following specific examples.

EXAMPLES

25 (A) Preparation of Activated Unsaturated Group-Containing Compounds

(A1) Into a reactor were added 1750,0 parts by weight (pbw) of xylene, which were heated to boiling temperature. Next was
30 added, over a period of three hours, a mixture of
1400,0 pbw of glycidyl methacrylate,
1935,5 pbw of styrene,
164,5 pbw of butyl acrylate, and

186,5 pbw of tert.butyl peroxy-3,5,5-trimethylhexanoate (commercially available under the trade designation Trigonox 42S from Akzo Chemicals), and thereafter an additional 194,0 pbw xylene. The reaction mixture was kept at boiling temperature until a conversion of at least 98% was achieved.

To this first reaction product was added

645,5 pbw of acrylic acid, *reacts with* Δ —

6,0 pbw of hydroquinone monomethylether and

1,5 pbw of chromium(III) 2-ethylhexanoate (commercially available under the trade designation Cordova AMC-2 from Cordova Chemicals),

and this mixture was reacted at 120°C under throughput of air until the acid value had decreased below 1.

After addition of 1361,0 pbw of xylene and 367,0 pbw of n-butanol, a 53,2 wt% polymer solution was obtained with a viscosity of 85,7 cPa.s at 20°C, a color of 250 Apha, an acid value of 0,1 and an Mn of 3580.

(A2) Into a five liter reaction vessel equipped with a thermometer, stirrer, air sparge and condensor, were charged 1445,6 pbw of isophorone diisocyanate, 160,9 pbw of dry methyl isobutyl ketone, 1,4 pbw of dibutyltin dilaurate and 0,9 pbw of 2,6-di-tert.butyl p-cresol (commercially available under the trade designation Ionol CP from Shell). After heating the mixture under stirring to a temperature of 60°C, 1432,6 pbw of 2-hydroxyethylacrylate were added continuously over a period of one hour while a maximum temperature of 65°C was maintained by cooling. Subsequently, 0,7 pbw of dibutyltin dialurate dissolved in 6,3 pbw of dry methyl isobutyl ketone were added dropwise over a period of ten minutes, followed by another 420,8 pbw of dry methyl isobutyl ketone.

The reaction mixture was thereafter maintained at 65°C for four hours, after which the NCO content of the remaining solution was about 0,5%. 192,4 pbw of n-butanol were then added, and the reaction mixture maintained at 65°C until an NCO content of less than 0,1% was achieved (about another two hours).

5

After cooling to room temperature, an almost colorless solution of a urethane diacrylate was obtained with a non-volatiles content of 79,3% and a viscosity of 900 mPa.s.

10

(B) Preparation of Activated CH Group-Containing Compounds

15

(BI) In a reactor, 560,0 pbw of Solvesso 100 were heated to a temperature of 160°C. Subsequently, over a period of three hours, there was added a mixture of 1336,4 pbw of acetoacetoxyethylmethacrylate, 113,2 pbw of butylacrylate and 550,4 pbw of styrene. Separately from the monomer mixture there was added, over a period of three hours and fifteen minutes, a mixture of 200,0 pbw of Solvesso 100 and 200,0 pbw of Trigonox 42S.

20

25

After addition of the peroxide solution, the reaction mixture was cooled to 140°C and an additional peroxide solution of 50,0 pbw of Solvesso 100 and 10,0 pbw of Trigonox 42S was added. Subsequently, after 30 and 60 minutes, further peroxide solutions of 10,0 pbw of Solvesso 100 and 10,0 pbw of Trigonox 42S were added.

30

After an additional two hours of reaction, the mixture was cooled. Obtained was a polyacetoacetate resin solution with a viscosity of 117 cPas and a solids content of 66,7%. The polyacetoacetate resin possessed an acid number of 2, a theoretical acetoacetate number of 175 and a number average molecular weight (via GPC) of 1270.

(C) Preparation of Blocked Catalysts

(C1) To a solution of 35,5 grams of phenylglyoxylic acid in 150,0 grams tetrahydrofuran were added dropwise 36,0 grams of 1,8-diaza-bicyclo[5.4.0]undec-7-ene. After stirring for thirty minutes, the salt was isolated by evaporation of the solvent.

The recovered salt was purified by means of recrystallization from a solution in 40 ml tetrahydrofuran, yielding a pale yellow salt in a yield of about 67%.

(C2) The procedure of (C1) was repeated, except that the phenyl glyoxylic acid was replaced with 52,5 grams of 9-anthracene carboxylic acid.

Example 1 and Comparative Example 1

A coating composition was prepared from 30,0 grams of (A1), 16,5 grams of (B1), 3,4 grams of butylacetate and 9,8 grams of a 10% solution of (C1) in a mixture of butylacetate/methanol (87,5/12,5).

As a comparison, the same coating composition was formulated but instead of the solution of (C1) was utilized 4,9 grams of a 10% solution of 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU) in butylacetate.

These compositions were tested for geltime by storing 100 grams of the reaction mixture in a closed tin at a temperature as set forth below. The geltime is reported as the time when the mixture no longer flowed as a liquid upon stirring with a spatula.

Further, both compositions were applied onto a tin plated steel panel with a drawbar to a dry layer thickness of ca. 50 μ m.

The panel of Example 1 was irradiated with a 400 Watt mercury lamp at a distance of 38 cm. The panel of Comparative Example 1 was not irradiated.

5 The petrol resistance of the so-applied coatings was tested qualitatively. After one week cure at 23°C a drop of petrol was applied to the test panel. After five minutes, the panel was inspected for coating softening.

10 The pendulum hardness of the so-applied coatings was also tested after one day and one week cure at 23°C with the aid of a Persoz apparatus.

The following results were obtained:

15		<u>Geltime</u>	<u>Petrol Resist.</u>	<u>Persoz Hard. 1 day</u>	<u>Hard. 1 week</u>	<u>Dry Layer Thickness</u>
	Example 1	>1 week at 50°C	O.K.	35"	137"	51µm
20	Comp. Examp.1	10 min. at 20°C	O.K.	31"	115"	57µm

Example 2 and Comparative Example 2

25 Example 1 was repeated except that 25 grams of (A2), 33 grams of (B1) and 13,4 grams of the 10% solution of (C1) were utilized.

Comparative Example 1 was also repeated except that 6,75 grams of the 10% solution of DBU was utilized.

The following results were obtained:

	<u>Geltime</u>	<u>Petrol Resist.</u>	<u>Persoz 1 day</u>	<u>Hard. 1 week</u>	<u>Dry Layer Thickness</u>
Example 2	>10 days at 50°C	good	123"	249"	45 μ m
Comp. Examp.2	22 min. at 20°C	good	140"	232"	48 μ m

Example 3 and Comparative Example 3

The composition of Example 1 was repeated except that the solution of (C1) was replaced with 12,1 grams of a 10% solution of (C2) in a mixture of butylacetate/methanol (87,5/12,5).

This composition and the composition of Comparative Example 1 were applied onto a tin plated steel panel with a drawbar to a dry film thickness of ca. 80 μ m. For each composition two panels were prepared. One of each was exposed to daylight, while the other was stored in darkness. The petrol resistance and pendulum hardness were measured as above.

The following results were obtained:

	<u>Petrol Resist.</u>	<u>Persoz 1 day</u>	<u>Hard. 1 week</u>	<u>Dry Layer Thickness</u>
Example 3 - light	O.K.	12"	116"	86 μ m
Example 3 - dark	N.O.K.	no curing		----
Comp. Examp.3 -light	O.K.	21"	130"	78 μ m
Comp. Examp.3 - dark	O.K.	20"	128"	82 μ m

Claims

1. A coating composition comprising (A) an activated unsaturated group-containing compound, (B) an activated CH group-containing compound and (C) a basic catalyst, characterized in that the basic catalyst (C) is blocked with an acidic compound whereby the so-blocked catalyst becomes unblocked under the influence of UV light having a wavelength in the range from 250-500 nm.
2. The coating composition according to claim 1, characterized in that the acidic compound is selected from (a) α -keto carboxylic acids; (b) aromatic or N-heterocyclic substituted formic, acetic and oxyacetic acids; and (c) halide compounds.
3. The coating composition according to claim 1 or claim 2, characterized in that the basic catalyst (C) comprises a nitrogen base.
4. The coating composition according to claim 3, characterized in that the basic catalyst is selected from amine and ammonium compounds.
5. The coating composition according to claim 1 or claim 2, characterized in that the basic catalyst comprises a phosphane.
6. The coating composition according to any one of claims 1-5, characterized in that the acidic compound is utilized in an amount of from 10 to 125 equivalent percent required to neutralize the basic catalyst.

7. The coating composition according to claim 6, characterized in that the acidic compound is utilized in an amount of from 25 to 125 equivalent percent required to neutralize the basic catalyst.
- 5 8. The coating composition according to claim 7, characterized in that the acidic compound is utilized in an amount of from 50 to 100 equivalent percent required to neutralize the basic catalyst.
- 10 9. The coating composition according to any one of claims 1-8, characterized in that the strong basic catalyst (C) and acidic compound together comprise a salt.
- 15 10. The coating composition according to any one of claims 1-9, characterized in that (A) and (B) are contained in an amount such that the ratio of the number of activated CH groups to the number of activated unsaturated groups is in the range of 0,25 to 4,0.
- 20 11. The coating composition according to any one of claims 1-10, characterized in that the basic catalyst (unblocked) is utilized in an amount ranging from 0,05 wt% to 3,0 wt%, based upon the combined weight of (A) and (B).
- 25 12. A decorative coating based upon the coating composition according to any one of claims 1-11.
- 30 13. A method of coating a substrate by applying a coating composition as set forth in any one of claims 1-12, then curing the same at least in part by exposure to UV light of a wavelength in the range of 250-500 nm.

14. A basecoat/clearcoat system, characterized in that the clearcoat is based upon the coating composition according to any one of claims 1-11.

5 15. A method of coating a substrate with the basecoat/clearcoat system of claim 14 by applying the basecoat onto the substrate, applying the clearcoat over the basecoat then curing the same, characterized in that curing of the clearcoat is at least in part by exposure to UV light of a wavelength in the range of 250-500 nm.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 94/01451

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C09D4/00 C08F2/48 C09D4/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C09D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 448 154 (AKZO) 25 September 1991 cited in the application ----	1-4
A	EP,A,0 160 824 (HOECHST) 13 November 1985 cited in the application & US,A,4 871 822 ----	1,5
A	EP,A,0 008 626 (BAYER) 19 March 1980 cited in the application & US,A,4 369 206 ----	1-2
A	EP,A,0 027 891 (BAYER) 6 May 1981 cited in the application & DE,A,29 40 333 -----	1-2

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. onal Application No

PCT/EP 94/01451

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0448154	25-09-91	JP-A- 4222879 US-A- 5219958	12-08-92 15-06-93
EP-A-0160824	13-11-85	DE-A- 3508399 AU-B- 572640 AU-A- 4080785 CA-A- 1281494 JP-A- 60226525 US-A- 5084536 US-A- 4871822	17-10-85 12-05-88 10-10-85 12-03-91 11-11-85 28-01-92 03-10-89
US-A-4871822	03-10-89	DE-A- 3508399 AU-B- 572640 AU-A- 4080785 CA-A- 1281494 EP-A,B 0160824 JP-A- 60226525 US-A- 5084536	17-10-85 12-05-88 10-10-85 12-03-91 13-11-85 11-11-85 28-01-92
EP-A-0008626	19-03-80	DE-A- 2830953 JP-A- 55022669 US-A- 4369206	24-01-80 18-02-80 18-01-83
US-A-4369206	18-01-83	DE-A- 2830953 EP-A,B 0008626 JP-A- 55022669	24-01-80 19-03-80 18-02-80
EP-A-0027891	06-05-81	DE-A- 2940333 JP-A- 56081532	07-05-81 03-07-81
DE-A-2940333	07-05-81	EP-A,B 0027891 JP-A- 56081532	06-05-81 03-07-81